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EMISSION SPECTROSCOPY OF CCl_4 AND BCl_3 PLASMAS DURING ALUMINUM ETCHING

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ABSTRACT

Spectroscopy of BCl_3 and CCl_4 plasmas shows major differences that can be related to their etch characteristics. BCl_3 alone etches Al_2O_3 readily, but etches aluminum slowly. Adding Cl_2 reduces its effectiveness at etching Al_2O_3, but allows a very rapid aluminum etch. The spectra of CCl_4 plasmas do not reveal major differences in chemistry with the addition of Cl_2. From spectral evidence the main difference between the two gases is that CCl_4 is a much better source of atomic chlorine than is BCl_3. Plasmas of CCl_4 alone, CCl_4 plus Cl_2, and BCl_3 plus Cl_2 show a strong band emission at 257 nm due to Cl_2. This band can obscure the 261 nm band of AlCl that is often used as an endpoint signal. The intensity of this band is very sensitive to the presence of aluminum in the plasma. The Cl_2 signal is quenched after etch initiation, when AlCl emission is detected. As the slice clears and the AlCl emission disappears, the Cl_2 signal returns. The Al atomic emission lines at 394 and 396 nm have no interference and are suggested as better lines for end point detection.

Introduction

Plasma spectroscopy offers an excellent window into the mechanism of plasma etching. This is particularly true when the etch has a large chemical component. In that case the plasma will emit the characteristic spectral emissions of both reactant and product species. This is already widely used in endpoint detection in silicon (1) and aluminum etching (2). This paper will examine the plasma emission spectra toward elucidating etching mechanisms of various gases in aluminum processing.

Two commonly used gases in Al thin film etching are CCl_4 and BCl_3, either alone or in combination with Cl_2. Ar or He is usually added as a diluent. These gases show great differences in their spectral characteristics, especially in the region between 250 and 400 nm. Emissions from reactant gas fragments as well as Cl_2, Al, and AlCl are

observed in this region (3). Atomic Cl can be detected at 726 nm. These spectra can be related to their etching properties. Furthermore, examination of traces of both AlCl and Al emission during etching shows significant differences that should be taken into account in selecting an end point signal.

Experimental

All data reported here were obtained with a load-locked parallel plate plasma reactor with an anodized aluminum interior. Spectra were recorded with a quarter meter monochromator with 2 nm resolution. All plasma conditions were at 1.0 torr with 13.56 MHz excitation.

Results and Discussion

The spectrum of 1% CCl_4 in Ar shows bands due to Cl_2 at 257, 308 nm and CCl at 272-279 nm. No Al or AlCl emission is observed when the plasma is sustained in an empty anodized aluminum etch chamber. The addition of a small amount of Cl_2 equal to the CCl_4 in the plasma causes the CCl emission to be greatly reduced while emissions from Cl_2 and Cl grow in intensity.

The spectrum of 2% BCl_3/Ar in an empty anodized aluminum chamber shows several major differences over the CCl_4 plasma. No Cl_2 emission is seen, and atomic Cl emission is weaker than with CCl_4. BCl emission between 266 and 285 nm is very strong. The band of AlCl at 261 nm is seen with strong intensity, as are strong aluminum lines at 394, 396 nm, and weak aluminum lines at 308, 309 nm. The addition of a small amount of Cl_2 to the plasma removes any emission due to Al species, reduces the BCl emission, and results in strong Cl_2 emission.

BCl_3 is regarded as an excellent etch initiator with a rapid etch rate of native aluminum oxide. The spectral data corroborate this, since the presence of Al and AlCl emission from an anodized aluminum chamber is direct evidence of etching of aluminum oxide. The absence of Al emission from the empty chamber when CCl_4 is used suggests that BCl_3 is a much better aluminum oxide etchant than is CCl_4. This is in contrast to a published report that states that CCl_4 is a faster etchant for aluminum oxide than is BCl_3 (4). Moisture contamination could not have been the reason for this difference since the load locks on the reactor always provided very reproducible etch initiation with both BCl_3 and CCl_4. The addition of Cl_2 to the BCl_3 plasma suppresses Al emission, indicating that oxide etching becomes inefficient in the presence of added Cl_2. However, because of the overlapping of the broad 257 nm band of Cl_2 with the 261 nm band of AlCl, this correlation is not clear. To test this a silicon slice with an aluminum thin film was etched while the plasma spectrum was repetitively scanned

between 255 and 265 nm to monitor both Cl_2 and AlCl emission. This is shown in Figure 1. Simultaneously the emission at 395 ± 3 nm was monitored to follow the Al atomic emission lines. This is shown in Figure 2. The atomic emission shows a steep onset and drop off as the slice clears. The 255-265 nm region shows an interesting quenching effect. During the induction period before the penetration of the native oxide film, Cl_2 emission is very strong and no AlCl signal is observed. The appearance of the AlCl signal is accompanied by the decrease and disappearance of the Cl_2 signal. As the slice clears, the process is reversed. This behavior suggests caution in using the 261 nm band of AlCl as an end point for Al etch. The fall of one signal and rise of another overlapping signal could obscure the end point trace.

From the spectral data, BCl_3/Ar is an excellent etch gas for aluminum oxide. However, when aluminum coated slices are etched with BCl_3, the etch is very slow unless Cl_2 is added. However, the disappearance of the Al emission from the empty chamber suggests that the addition of Cl_2 to a BCl_3/Ar plasma reduces the effectiveness of BCl_3 in etching oxide. In both the BCl_3 and CCl_4 plasmas, the addition of Cl_2 suppresses dissociation of the other molecule, causing fewer of the active radicals (either BCl or Cl) to be produced. Adding Cl_2 to BCl_3 apparently nullifies one of the advantages ascribed to BCl_3 plasmas, namely its excellent etch initiation (oxide penetration) characteristics. However, the addition of Cl_2 is necessary to enhance the etch rate of an aluminum film.

The etching characteristics of CCl_4 do not appear to be changed quite so drastically by the addition of Cl_2. CCl_4/Ar alone apparently produces considerable amounts of free chlorine as well as sufficient Cl radicals to penetrate the oxide and initiate etch. Addition of Cl_2 increases the atomic Cl concentration and accelerates the etch. A CCl_4 plasma does not etch the anodized aluminum chamber at a spectroscopically detectable rate.

A particularly interesting feature of the spectra of aluminum etch plasmas is the behavior of the Cl_2 band emission at 257 μm. The Cl_2 emission is highly sensitive to the onset and completion of the etch. This behavior is contrasted to that of the atomic Cl emission line at 726 nm. When the Cl emission was monitored during etching under the same conditions as Figure 1, the Cl signal dropped by about 25% after etch initiation, and rose to its original level as the film cleared. Simple depletion of chlorine species does not account for the loss of the Cl_2 signal.

The 257 nm band of Cl_2 is a known bond-to-bond transition originating above the dissociation energy of the chlorine molecule (5). The upper state is ionic in character and the lower state is covalent. The upper state is efficiently pumped by the discharge. The AlCl band originating at 261 nm provides a non-radiative path for

quenching the excited Cl_2. Another similar band of Cl_2 occurs at 308 nm. It is readily observed in the absence of aluminum species in the plasma. Like the 257 nm band, it is quenched by the presence of Al species. In this case, the quenching species is probably the Al atom resonance state originating at 308 nm.

The 261 nm band of AlCl is widely reported as a suitable endpoint signal for aluminum etching. However, the behavior of the overlapping 257 nm Cl_2 band suggests caution in its use. The opposing behavior of the two signals can make the endpoint ambiguous. A preferable signal for CCl_4 or BCl_3 plasmas are the Al lines at 394 and 396 nm. No other lines in the region between 390 and 400 nm are detected with either He or Ar diluents. This allows for use of an interference filter to isolate the two lines. As shown in Figure 2, they produce a sharp endpoint under conditions where 261 nm can be ambiguous.

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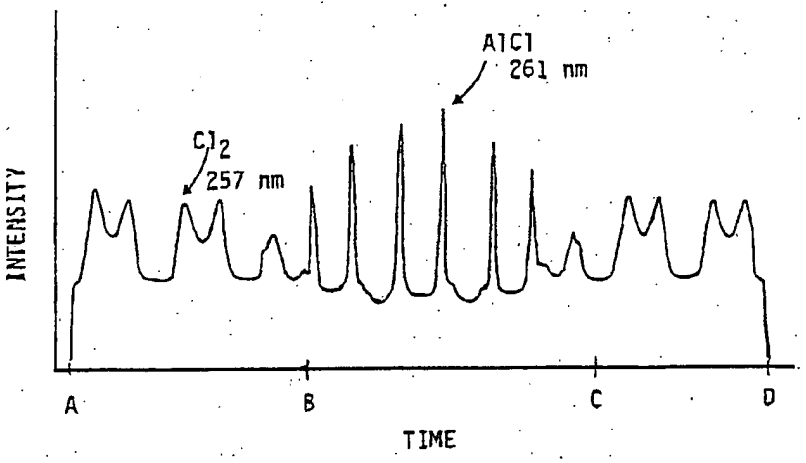

Figure 1.

Repetitive scan during etching an aluminum coated wafer with BCl_3/Ar. The spectrum was repetitively forward and reverse scanned between 255 and 265 nm. The broad band is Cl_2 emission centered at 257 nm and the sharp spike is due to AlCl at 261 nm. During the induction period (A to B) only Cl_2 is observed. During etching (B to C) only AlCl is oberved. After the slice clears (C, only Cl_2 emission is observed. RF is turned off at point D.

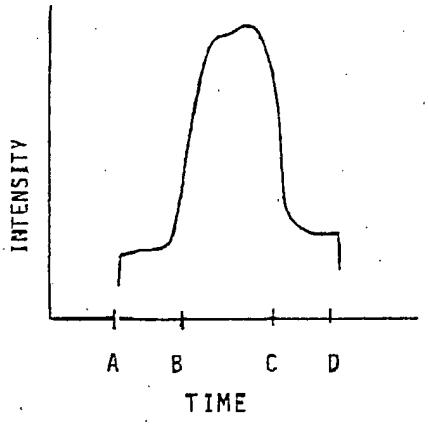

Figure 2.

Trace of the signal generated at 395 nm and recorded simultaneously with the trace shown in Figure 1. Signal was detected through a 5 nm half bandwidth interference filter to detect both aluminum lines at 394 & 396 nm. Time scale is compressed by a factor of 3.5 compared to Figure 1. Points A, B, C, D correspond to RF on, etch initiation, etch termination, and RF off, respectively.